

CaOH has a second linear structure HCaO

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The energy surface of CaOH has been studied and an isomer of the form of HCaO with an electronic state of ${}^2\Sigma^+$ symmetry has been found. It is linear with H–Ca and Ca–O bond lengths of 2.021 and 2.002 Å, respectively, at the CISD level with a basis set of triple-zeta plus double polarization quality. The overall electronic structure is largely ionic and can be described as $H(1s^2)Ca(4s^0)O(2s^22p_x^22p_y^22p_z^1)$ ($H^-Ca^{2+}O^-$). The minimum on the energy surface is well defined and the harmonic vibrational frequencies have been calculated. The O–H bond length and stretching frequency and the bending frequency of CaOH have also been calculated and compared with experiment. © 1995 American Institute of Physics.

I. INTRODUCTION

The gas-phase alkaline earth monohydroxides are of considerable astrophysical interest. Tsuji¹ has predicted that these compounds are important species in stellar atmospheres. This interesting class of free radicals provides a number of ideal candidates for optical studies since they are readily produced in the laboratory and their low-lying electronic states are located in a convenient region for dye laser excitations. In 1983, Harris and co-workers performed the first rotational analysis of CaOH/CaOD² and SrOH/SrOD³ and established the linear geometry of these molecules. They used a molecular source operating at low temperature and low pressure which greatly reduced the spectral density. Since then, spectroscopic investigations of MOH (M=Mg, Ca, Sr, and Ba) molecules^{4–14} have progressed rapidly. In particular, extensive and high precision data for CaOH and SrOH have been recorded in several laboratories, yielding important physical quantities such as permanent electric dipole moments,⁸ and the Renner–Teller and Fermi resonance parameters.^{10,13,14} The simultaneous study of the two isotopomers, CaOH and CaOD, has led to accurate determination of the equilibrium bond lengths, valence force constants and Coriolis coupling parameters for the ground state.¹⁴

The geometries and electronic structures of CaOH and other alkaline earth monohydroxides have also been subject to various theoretical studies. It has been well established that like the molecules consisting of alkaline earth metals and other electronegative ligands (*L*), they are essentially ionically bonded as $M^+(OH)^-$. The metal gives one *s* electron to the ligand and the two parts are held together electrostatically. This picture is consistent with the experimental observations and the theoretical studies which indicate that all of these molecules are linear or quasilinear. The linearity suggests that the bonding is ionic, for otherwise the lone pairs on oxygen would force the molecules to bend if the bonding were covalent. The low-lying electronic states are formed by promoting the unpaired electron from the *ns* orbital of the metal to the *np(n–1)d* and the $(n+1)s$ orbitals. Based on this model, a substantial amount of theoretical work with *ab initio* and semiempirical methods has been done. Bauschlicher and Partridge calculated the dissociation energy of CaOH and LiOH using the restricted open-shell

Hartree–Fock (ROHF) method with a large basis set of at least triple-zeta plus double polarization quality, assuming that the molecules will dissociate into ions.¹⁵ Bauschlicher *et al.*¹⁶ studied the structures and energetics of the ground states of the alkali and alkaline–earth monohydroxides including CaOH at the singles plus doubles configuration interaction (CSID) level with the same basis set. In addition to the equilibrium distance between the metal and the ligand and the dissociation energy, vibrational frequencies and bending potentials were also calculated. The permanent dipole moments of the $X^2\Sigma^+$, $A^2\Pi^+$, and $B^2\Sigma^+$ states of CaOH were calculated at the computed equilibrium geometries with the coupled-pair functional (CPF) and modified CPF methods.¹⁷ The geometries and bending potentials of BeOH and MgOH were also studied using unrestricted-Hartree–Fock fourth-order Møller–Plesset perturbation theory by Palke and Kirtman.¹⁸ Ortiz studied the ground and excited states of CaL (L=CH₃, NH₂, OH, and F) by means of electron propagator calculations.¹⁹ Semiempirical models were proposed^{20–23} to calculate the binding energies, excitation energies, and dipole moments of these ionic molecules M^+L^- including L=OH[–]. The models were based on the classic electrostatic interaction plus the polarization of M^+ and L^- and the excited states were treated in a fashion closely related to ligand field theory. The predictions compared well to experimental and *ab initio* data.

During our recent study of the energy surface of CaOH another minimum was found with an electronic state of ${}^2\Sigma^+$ symmetry. It has the form HCaO with a linear structure, analogous to HBO and HAIO. In this paper, we describe the energy surface around the minimum at both the Hartree–Fock and the CISD levels. Also included are the O–H stretching frequency and the bending frequency of CaOH, which were omitted from previous theoretical studies.

II. COMPUTATIONAL METHODS

The basis set used for most of the calculations is fairly complete: (15s13p7d2f/9s9p6d2f) for Ca, (11s7p3d1f/6s4p3d1f) for O, and (8s4p/5s3p) for H as in the Bauschlicher *et al.* studies^{15,16} which should be consulted for complete details. The calculations were first done at the ROHF level, followed by the CISD calculations to include

the correlation effects for the valence-shell electrons on all the atoms, plus the outercore $3s^2, 3p^6$ electrons of Ca. The study on alkaline-earth monohalides²⁴ has shown that the pair-pair terms, the double excitations where one electron is excited from a M^+ outer-core orbital and the other from a L^- valence orbital, are increasingly important when the M-L distance is small and tends to make the bond short. Including the outer-core shell electrons (17 electrons in total) in correlation calculations compensates for the correlation effect of valence electrons that tends to make the bond too long and yields results in better agreement with experiment for the M-L bond length, frequency and dissociation energy. In the CI calculations, the contributions of all configurations from double excitations were estimated by means of perturbation theory and those that are predicted to make contributions below a threshold (10^{-7} hartree for bond stretching modes) were eliminated from the diagonalization of the Hamiltonian matrix to save disk space and computing time.^{25,26} The estimated contribution from the discarded configurations changed little during optimization for bond-stretching modes.

For the CISD bending potential scan, the estimated contribution from the discarded configurations changes with the angle and becomes increasingly significant. Because of hardware limitations a somewhat smaller basis set was used. It is basically a triple-zeta-valence (TZV) basis set augmented with diffuse and polarization functions. The basis functions for H are from Dunning's TZV basis set²⁷ augmented with a diffuse s function and three sets of p polarization functions, resulting in a basis set $(6s3p/4s3p)$. The $(11s7p3d/6s4p3d)$ set for O is composed of Dunning's TZV, a diffuse s , a diffuse set of p and three sets of d polarization functions. The Ca set starts from Wachters' $(14s9p)$ set²⁸ contracted to $(8s4p)$, augmented with three sets of p functions to describe the subshell $4p$, and three sets of d polarization functions, resulting in $(14s12p3d/8s7p3d)$. The energy threshold for selecting configurations included in the Hamiltonian diagonalization was also decreased to 5.0×10^{-8} hartree. With this basis set, the estimated contribution from the discarded configurations was less than 10^{-5} hartree and had little effect on the geometry optimization.

The equilibrium bond distances and harmonic frequencies were obtained by a parabolic fit to the energy curves with step intervals less than 0.03 \AA . The bending angle was scanned up to 15° from the linear structure. The calculations were done with the GAUSSIAN92/ DFT²⁹ and MELDF-X programs.³⁰

III. RESULTS

A. ROHF

Optimization of linear HCaO yielded 2.073 \AA for H-Ca and 2.028 \AA for Ca-O at the ROHF level. SCF convergence failure with GAUSSIAN92 prevented characterization of the stationary point by frequency analysis. A potential scan of the bond angle using MELDF-X at the optimized bond lengths of the linear structure confirmed that the linear structure is a minimum. The H-Ca and Ca-O harmonic stretching frequencies and the harmonic bending frequency were

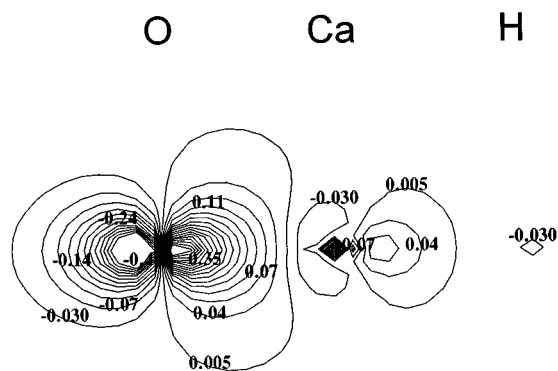


FIG. 1. Contour plot of the singly occupied orbital of HCaO.

computed to be 1324 , 560 , and 108 cm^{-1} , respectively. CaOH was also calculated at the ROHF level for comparison. In contrast to CaOH where the unpaired electron is on Ca, the unpaired electron of HCaO is mainly of oxygen $2p_z$ character, which is also the bonding orbital between Ca and O. The contours of the singly occupied orbital of HCaO corresponding to the bonding between Ca and O are depicted in Fig. 1. The Mulliken population analysis gave -0.69 , 1.47 , and -0.77 , respectively, for H, Ca, and O, showing that the amount of negative charge hydrogen gains is quite large, close to what the oxygen does, although one might expect a larger difference as the latter is much more electronegative. Since the number of electrons lost by Ca in HCaO is close to twice that (0.79) in CaOH, one can argue that Ca in HCaO loses two electrons, one each to hydrogen and oxygen. Figure 2 shows the doublet occupied molecular orbital corresponding to the bonding between H and Ca. The molecular orbital is dominated by the contribution of the hydrogen s basis functions. The calculation also shows that the negative charges on both hydrogen and oxygen increase as the bond lengths increase. Therefore, the H-Ca and Ca-O bonds are largely ionic. The overall HF electronic structure can be symbolized as $H(1s^2)Ca(4s^0)O(2s^2 2p_x^2 2p_y^2 2p_z^1)$ or $H^-Ca^{2+}O^-$.

B. CISD

The geometries and harmonic frequencies of HCaO and CaOH at the CISD level along with experimental results for

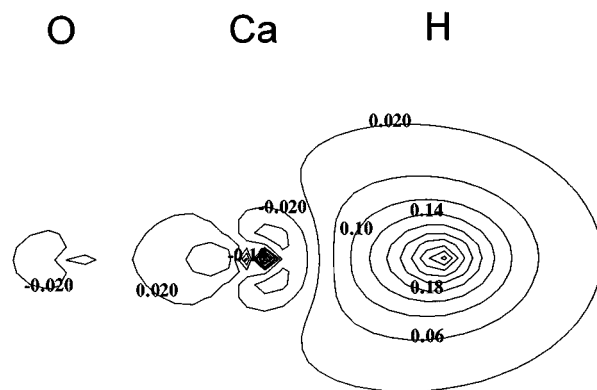


FIG. 2. Contour plot of the bonding orbital between H and Ca.

TABLE I. The total CISD energies, equilibrium bond lengths, and harmonic frequencies of HCaO and CaOH. The CISD result includes 17 electrons unless noted otherwise.

HCaO (theory)	CaOH (theory)	CaOH (experiment, Ref. 10)
$E_{\text{total}} = -752.41773$ hartrees	-752.52027 hartrees ^a	
$R(\text{H}-\text{Ca}) = 2.021 \text{ \AA}$	$R(\text{O}-\text{H}) = 0.948 \text{ \AA}$	0.954 \AA
$R(\text{Ca}-\text{O}) = 2.002 \text{ \AA}$	1.988 \AA (Ref. 16)	1.975 \AA
$\omega(\text{H}-\text{Ca}) = 1288 \text{ cm}^{-1}$		
$\omega(\text{Ca}-\text{O}) = 515 \text{ cm}^{-1}$	629 cm^{-1} (Ref. 16)	617 cm^{-1}
$\omega(\text{H}-\text{Ca}-\text{O}) = 170 \text{ cm}^{-1}$	$\omega(\text{Ca}-\text{O}-\text{H}) = 405 \text{ cm}^{-1}$	354 cm^{-1}
$\omega(\text{H}-\text{Ca}-\text{O}) = 146 \text{ cm}^{-1}$	$\omega(\text{Ca}-\text{O}-\text{H}) = 380 \text{ cm}^{-1}$ (nine electrons)	
	$\omega(\text{O}-\text{H}) = 4040 \text{ cm}^{-1}$	

^aCalculated at the geometry of Ref. 16.

CaOH are listed in Table I. Compared with the ROHF results, the H–Ca bond length is shortened by 0.052 \AA , and Ca–O bond length by 0.026 \AA . This is similar to the CaOH case where the Ca–O bond length was shortened by 0.018 \AA when the electron correlation was included.¹⁶ Relative to the Ca–O bond in CaOH, the Ca–O bond in HCaO is slightly longer and has a lower frequency, indicating that the latter is weaker (since hydrogen is very light, the Ca–O stretching frequency can be used to compare the Ca–O bond strengths of HCaO and CaOH).

To understand the H–Ca bond it is helpful to compare with the bond length and frequency of the CaH molecule. The experimental values³¹ for CaH are 2.0025 \AA and 1298.34 cm^{-1} , respectively, which are comparable with those of the H–Ca bond in HCaO, 2.021 \AA and 1288 cm^{-1} respectively, suggesting a similarity between them.

A potential energy scan of the H–Ca–O bond angle confirmed that the linear structure is a minimum at the CISD level, which reinforces the conclusion at the ROHF level that the linear structure is energetically favored. In fact, the curvature at the CISD level is greater than at the HF level as indicated by the greater bending frequency (170 cm^{-1} vs 151 cm^{-1} with the TZV basis set) at the CISD level.

The previous theoretical studies of MOH have been focused on characterizing the Ca–O bond with the O–H bond length fixed at its value in free OH^- . In this work, we calculated the potential curve for the O–H stretching mode. The optimized bond length is slightly (0.006 \AA) shorter than experimental result, and the frequency is much higher than that of free OH or OH^- which is around 3700 cm^{-1} .³² The increase of the O–H frequency from a free anion to a ligand in MOH should not be surprising as M^+ would make OH^- more polarized.

Since the experimental value of the CaOH bending frequency is available, theoretical calculations were carried out for comparison. It is found that the bending frequency of CaOH calculated with 17 electrons included in CISD procedure was about 50 cm^{-1} higher than the experimental value (354 cm^{-1}). The CISD value (380 cm^{-1}) including valence shell electrons only (nine electrons), however, has been found to be in better agreement with experiment. The energy difference between the two structures HCaO and CaOH is

large (269 kJ/mol), which may help to explain why HCaO has not been observed.

IV. CONCLUSION

A second structure, HCaO with a $^2\Sigma^+$ state has been found on the hypersurface of CaOH. It is linear and the H–Ca and Ca–O bond lengths are 2.021 and 2.002 \AA respectively. These were calculated at the CISD level with a basis set of at least triple-zeta plus double polarization quality. The overall electronic structure is largely ionic and can be described as $\text{H}(1s^2)\text{Ca}(4s^0)\text{O}(2s^22p_x^22p_y^22p_z^1)$. The H–Ca and Ca–O stretching frequencies and the bending frequency are listed in Table I. The H–Ca bond is similar to that of the HCa molecule as indicated by the similar bond length and frequency. The Ca–O bond in HCaO is longer and has a lower frequency than that in CaOH, suggesting that the former is weaker.

The O–H stretching potential has also been calculated and the stretching frequency was found to be much higher than that in the free OH radical and OH^- anion. The bending frequency of CaOH was obtained with different numbers of electrons included in the correlation calculations. It has been found that including valence electrons only yields results in better agreement with experiment.

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